# **PCT**

# WORLD INTELLECTUAL PROPERTY ORGANIZATION International Bureau



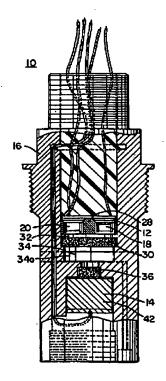
# INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> : G01N 27/26	A1	(11) International Publication Number: (43) International Publication Date:	WO 99/17110 8 April 1999 (08.04.99)
(21) International Application Number: PCT/US (22) International Filing Date: 24 September 1998 (		DE, DK, ES, FI, FR, GB, GI	
(30) Priority Data: 08/942,083 1 October 1997 (01.10.97)	,	Published  With international search repo	ort.
(71) Applicant: ANALYTICAL TECHNOLOGY, INC. 680 Hollow Road, Oaks, PA 19456 (US).	[US/U	<b>]</b> ;	·
(72) Inventors: CROMER, Raymond, B.; 873 Westtov West Chester, PA 19382 (US), SUMMERFIELD, D.; 4101 Tinder Hall Road, Phoenixville, P (US), FITZGERALD, Matthew, S.; 104 Arubi Schwenksville, PA 19473 (US).	Stepho A 194	n, 0	
(74) Agent: WASHBURN, Robert, B.; Woodcock Washb Mackiewicz & Norris LLP, 46th floor, One Libe Philadelphia, PA 19103 (US).	urn Ku rty Pla	2,	
· ·			

# (54) Title: COMBUSTIBLE GAS SENSOR WITH INTEGRAL HYDROGEN GENERATOR

#### (57) Abstract

An assembly (10) for verifying the response of a combustible gas sensor combining a catalytic combustible gas sensor (12) and a hydrogen generator (14) in one explosion proof housing (16).



# FOR THE PURPOSES OF INFORMATION ONLY

AL.	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	I.U	Luxembourg	SN	Senegal .
AU	Australia	GA	Gabon	1.V	Latvia	SZ	Swaziland
ΑŻ	Azerbaijan	GB	United Kingdom	MC	Мопясо	T'D	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
3 <b>B</b>	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav	TM	Turkmenistan
BF	Burkina Faso	GR	Greece		Republic of Macedonia	TR	Turkey
BC	Bulgaria	IIU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	II.	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CIF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	zw	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's	NZ	New Zealand		i i
CM	Cameroon		Republic of Korea	P).	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
Cz	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE.	Germany	LI	Liechtenstein	SID	Sudan		
DK	Denmark	LK	Sri Lanko	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

WO 99/17110 · PCT/US98/19844

## COMBUSTIBLE GAS SENSOR WITH INTEGRAL HYDROGEN GENERATOR

#### BACKGROUND OF THE INVENTION

#### 1. Field of the Invention

This invention relates to a method and apparatus for automatically testing
the response of combustible gas sensors and more particularly to a combustible gas
sensor with integral hydrogen generator.

#### 2. Description of the Related Art

Combustible gas sensors have been used for over fifty years to detect the presence of potentially hazardous concentrations of flammable gases or vapors. They are widely used in industry for safety purposes, providing a warning of potentially hazardous conditions before gas levels reach explosive levels. Commercial combustible gas sensors detect gases through the use of a heated catalytic element. When a combustible gas or vapor comes in contact with this element, the gas or vapor is burned, causing an increase in heat on that element. The resistance of the catalytic element changes in proportion to the combustion heat, and the resistance change is compared to a similar but inert reference element. In a typical catalytic gas detector, the catalytic element and the reference element form two legs of a simple Wheatstone bridge circuit which measures the resistance change caused by the presence of combustible gases and vapors. Combustible gas detectors are well known in the art and are described by

20 Warren J. Reilly in an article entitled "Combustible Gas Detectors" based on a paper

delivered at the Arrowspace/Test Measurement Conference, Philadelphia, 1975.

There are many manufacturers of this type of combustible gas sensor and the technology has been widely applied to leak detection applications in chemical and petrochemical plants, oil and gas exploration wells and platforms, and a variety of other industries where the potential for either leakage or buildup of potentially explosive levels of gas or vapor exist.

All combustible gas sensors using this technology suffer from the same basic problem, which is the slow, or in some cases, fast, passivation or chemical attack of the catalytic surface on which proper operation depends. This process occurs when sensors are exposed to air containing small amounts of silicone vapor, lead compounds, hydrogen sulphide, and organic vapors containing halogens that can form strong acids on the surfaces during the combustion process. Because combustible gas sensors are often used in ambient air environments where there can be no control over the types of poisoning agents that might be encountered, users of combustible gas sensors are required to manually check sensor operation on a regular schedule. Since sensors can be poisoned quickly when exposed to the wrong environment, frequent checking is desirable to insure the integrity of the detection system.

When a combustible gas sensor becomes poisoned, it looses sensitivity to the gases it is intended to measure. However, this poisoned condition is not detectable automatically because it appears to be the same as a properly operating sensor exposed to clean air. The only reliable sensor test is to manually expose a sensor to a combustible gas and observe the response.

Heretofore there have been attempts to automate this process by attaching external gas cylinders to the sensor and using a solenoid valve to periodically allow gas to flow to the sensor. However, this approach is expensive, made more so by the fact that the gas delivery system must be explosion-proof.

The combustible gas sensing system of the present invention provides the automatic checking of the combustible sensor every twenty four hours and greatly reduces the manual labor needed to verify that the gas detection system is operable and will respond in the event of gas leakage.

## SUMMARY OF THE INVENTION

Accordingly, the present invention is intended to obviate the above-described problems and has for its object to provide a system for verifying the response of a combustible gas sensor by combining the combustible gas sensor with an integral hydrogen generator in one explosion-proof assembly. The present invention provides an electrochemical hydrogen generator capable of delivering relative high H<sub>2</sub> concentrations (needed to properly test this type of sensor) to the combustible sensor, and integrating the generator into the sensor itself. The result is a device that includes both the sensor and a mechanism for automatically testing that sensor to detect loss of sensitivity.

Accordingly to one aspect of the invention there is provided an assembly for verifying the response of a combustible gas sensor including an explosion proof housing including a catalytic combustible gas sensor having active and passive sensing elements disposed within the housing. A hydrogen generator is disposed within the 15 housing and separated from the catalytic combustible gas sensor by a gas diffusion chamber. The gas diffusion chamber has an opening in the wall of the explosion proof housing to allow combustible gases in the ambient air to diffuse to the sensing elements of the catalytic combustible sensor. A sintered metal flame arrestor separates the combustible gas sensing elements from the combustible gas chamber and a sintered metal 20 flame arrestor separates the hydrogen generator from the combustible gas chamber. In another aspect of the invention, the hydrogen generator includes an electrochemical cell containing two embedded electrodes and a water based electrolyte, the electrolyte being a hygroscopic acid retained within a porous plastic medium within the hydrogen generator so that when water is electrolyzed to produce hydrogen, the water that is lost 25 is replenished by the humidity in the ambient air to insure sufficient water for the hydrogen generation process over an extended period of time.

In a further aspect of the invention there is provided a method including the steps of energizing the hydrogen generator of the aforesaid type to deliver a hydrogen test sample to produce a concentration above a predetermined lower explosive limit (LEL) within the gas diffusion chamber, causing the test gas to pass through the

sintered metal flame arrestor to a sensor cavity adjacent the catalytic combustible gas sensor, and monitoring the output of the combustible sensor during the gas generation cycle.

#### BRIEF DESCRIPTION OF THE DRAWINGS

- The present invention will be described in further detail with reference to the accompanying drawings.
  - Fig. 1 is an elevational view partly in section of a combustible gas sensor with integral hydrogen generator embodying the present invention.
- Fig. 2 is a schematic diagram of the electrical circuit in the combustible gas sensor with integral hydrogen generator illustrated in Fig. 1.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring to Fig. 1 there is disclosed an assembly 10 for verifying the

15 response of a combustible gas sensor. The assembly includes a catalytic combustible gas

sensor 12 and a hydrogen generator 14 both disposed within an explosion proof housing

16. The catalytic combustible gas sensor has an active element 18 and a passive element

20. The passive element 20 is sometimes referred to as a reference element and the

reference element 20 and active element 18 are arranged in a Wheatstone bridge. As

20 shown in Fig. 2 the active and passive elements 18 and 20 form two legs of the

Wheatstone bridge with the other two legs being formed by the resistors 22 and 24. The

circuit also includes an adjustable resistor 26. In operation combustible gas molecules

react, via a catalyst, to form oxidation products on the active (open to air) element 18

increasing its temperature and resistance. The sensing elements may be either coated

25 with a catalyst and coiled, or encased in a catalytic bead element, as well known in the

art.

As may be seen in Fig. 1 there is a thermal barrier 28, preferably made from Teflon, and positioned to keep the heat generated at the active element 18, when exposed to combustible gases, from transferring to the passive element 20, which does

5

- 5 -

not heat up on contact with combustible gases. A sintered metal flame arrestor 30 of stainless steel is positioned within the housing 16 to keep the sensing elements 18 and 20 isolated within the housing while allowing combustible gases to diffuse to a sensor cavity 32 adjacent to the sensing elements 18 and 20.

As may be seen in Fig. 1, the hydrogen generator 14 is mounted within the lower portion of the explosion proof housing 16 and is separated from the combustible gas sensor by a gas diffusion chamber 34. The gas diffusion chamber 34 has an opening 34a to the exterior of the housing 16. The gas diffusion chamber 34 is bounded by the sintered metal flame arrestor 30 which isolates the sensing elements 18 and 20 of the combustible gas sensor 12 and a second sintered metal flame arrestor 36 which isolates the hydrogen generator 14 from the gas diffusion chamber. The gas diffusion opening 34a allows ambient air and any combustible gases to diffuse into the chamber 34 of the housing 16 so that they are sensed by the active element 18 of the sensor. The hydrogen generator 14 is an electrochemical cell containing two embedded 15 electrodes 38 and 40, Fig. 2, and a water based electrolyte 42, Fig. 1. In operation, a 2.5 volts DC potential is placed across the electrodes 38 and 40 when the switch 44 is closed with the current being limited by resistor 46 to about 60mA. At this power level, water will be split into hydrogen and oxygen. The hydrogen is evolved from the surface of the electrode 38 nearest the diffusion opening and is allowed to move by natural 20 diffusion through the sintered metal flame arrestor 36, across the gas diffusion chamber 34 and through the sintered metal flame arrestor 30 into the sensor cavity 32 adjacent the sensing elements 18 and 20.

The hydrogen generator 14 relies on water inside the generator cell for hydrogen production. Since the generator cell must be relatively small from a packaging 25 standpoint, the amount of water could potentially limit a number of tests that could be run prior to the generator failing. Requiring generators to be refilled with water adds a maintenance requirement that particularly negates the value of the self-check. Formulating the electrolyte so that it pulls water out of the air allows the generator to run for well over a year without any type of service. Basically, the electrolyte is a 30 hygroscopic acid, such for example as concentrated sulfuric acid, which is retained inside a porous plastic medium similar to filter paper. When water is electrolyzed to

produce hydrogen, the water that is lost is replenished by the humidity in the ambient air.

In operation, the hydrogen generator 14 is activated on a periodic basis under software control for a fixed period of time. As may be seen in Fig. 2, hydrogen generator is activated when the switch 44 is closed. The switch 44 is microprocessor controlled. The current to the generator 14 is controlled to deliver a hydrogen concentration above 5% LEL (0.2% hydrogen by volume). Lower explosive limit (LEL) data for common combustible gases and vapors are published by the National Fire Protection Association. The LEL is the lowest concentration of the gas, mixed with air, which will propagate a flame. In normal air, the LEL can vary from 0.6% to 12.5%, by volume. Concentrations of gas above the LEL will propagate flame until the upper explosive limit (UEL) is reached. Above the UEL, gas concentrations are too rich to support combustion. The output of the combustible gas sensor 12 is monitored during the gas generation cycle. If the sensor output reaches a predetermined LEL value, normally 5%, the sensor is deemed to have passed the test and the hydrogen generator 14 is shut off. If the sensor does not reach the predetermined LEL value within a fixed time, the sensor 12 is deemed to have failed and an alarm signal is generated.

While a preferred embodiment of this invention has been illustrated, it is to be understood that other modifications thereof may be made within the scope of the appended claims.

10

#### What is claimed is:

- An assembly for verifying the response of a combustible gas sensor comprising an explosion proof housing, a catalytic combustible gas sensor having an active and a passive sensing elements disposed within said housing, and a hydrogen generator disposed within said housing and separated from said catalytic combustible gas sensor by a gas diffusion chamber, said gas diffusion chamber having an opening in the wall of said explosion proof housing to allow combustible gases in the ambient air to diffuse to said sensing elements of the catalytic combustible gas sensor.
  - The assembly according to claim 1 wherein a sintered metal flame arrestor separates said combustible gas sensing elements from said combustible gas chamber.
  - 3. The assembly according to claim 2 wherein a sintered metal flame arrestor separates said hydrogen generator from said combustible gas chamber.
- 4. An assembly according to claim 1 wherein said hydrogen generator comprises an electrochemical cell containing two embedded electrodes and a water based electrolyte.
  - 5. An assembly according to claim 4 wherein said electrolyte in said hydrogen generator is a hygroscopic acid retained within a porous plastic medium within said hydrogen generator so that when water is electrolyzed to produce hydrogen the water that is lost is replenished by the humidity in the ambient air to insure sufficient water for the hydrogen generation process over an extended period of time.
    - 6. The assembly according to claim 5 wherein said hygroscopic acid is

concentrated sulfuric acid.

- 7. In a system for verifying a response of a combustible gas sensor comprising an explosion proof housing, a catalytic combustible gas sensor having an active and a passive sensing elements disposed within said housing, and a hydrogen generator disposed within said housing and separated from said catalytic combustible gas sensor by a gas diffusion chamber, said gas diffusion chamber having an opening in the wall of said explosion proof housing to allow combustible gases in the ambient gas to diffuse to said sensing elements of the catalytic combustible gas sensor, and a sintered metal flame arrestor separating said combustible gas sensing elements from said combustible gas chamber, the method comprising the steps of energizing the hydrogen generator to deliver a hydrogen test sample to produce a concentration above a predetermined lower explosive limit (LEL) within the gas diffusion chamber, causing the test gas to pass through the sintered metal flame arrestor to a sensor cavity adjacent said catalytic combustible gas sensor, and monitoring the output of the combustible sensor
  - 8. The method according to claim 7 wherein the concentration in the gas diffusion chamber is above about 5% LEL.

1/2

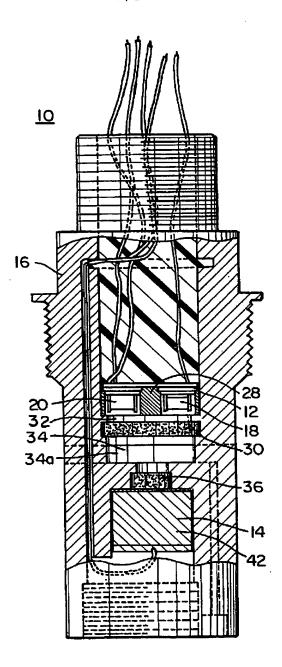
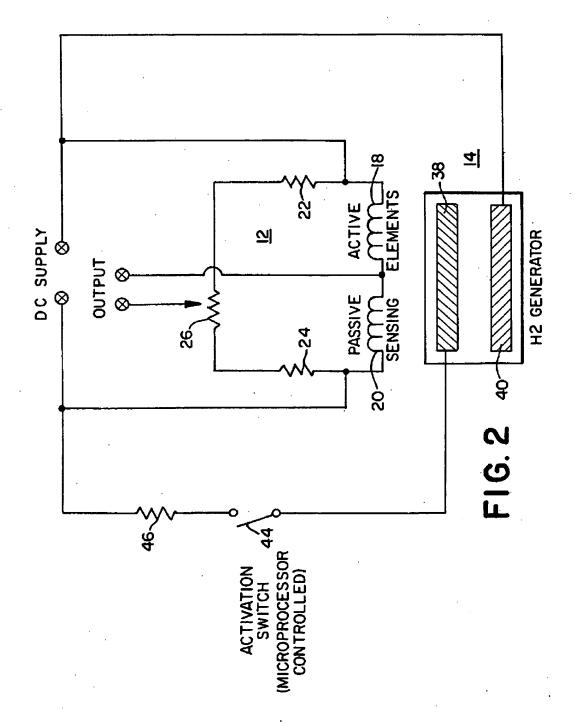


FIG. 1



## INTERNATIONAL SEARCH REPORT

International application No. PCT/US98/19844

	<u>'</u>						
A. CLASSIFICATION OF SUBJECT MATTER  IPC(6): G01N 27/26 US CL: 204/431							
According to International Patent Classification (IPC) or to both national classification and IPC							
B. FIEL	DS SEARCHED						
Minimum d	ocumentation searched (classification system followers)	ed by classification symbols)					
U.S. :	204/431, 401; 422/94, 95, 98; 436/152						
Documental	Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched						
Ì	Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  APS, CAS ONLINE						
C, DOC	UMENTS CONSIDERED TO BE RELEVANT		:				
Category*	Citation of document, with indication, where a	ppropriate, of the relevant passages	Relevant to claim No.				
Y	US 4,489,590 A (HADDEN) 25 Decem 5, lines 17-68, column 6, lines 1-35,	1-8					
Y	US 4,332,664 A (NOSZTICZIUS ET A column 1, lines 65-66, column 3, line	1-8					
Y	US 4,391,682 A (STRUCK et al.) 05 J 3, lines 4-40.	5, 6					
Y	US 4,155,712 A (TASCHEK) 22 May lines 15-32, column 2, lines 20-25.	1-3, 7, 8					
		•					
Furth	ner documents are listed in the continuation of Box (	C. See patent family annex.					
Special categories of cited documents:							
*A* document defining the general state of the art which is not considered to be of particular relevances  to be of particular relevances  date and not in conflict with the application but cited to understand the principle or theory underlying the invention							
	ther document published on or after the international filing date cument which may throw doubts on priority claim(s) or which is	*X* document of particular relevance; the considered novel or cannot be considered when the document is taken alone					
cited to establish the publication date of another citation or other special reason (as specified)  O document referring to an oral disclosure, use, exhibition or other		"Y" document of particular relevance; the considered to involve an inventive combined with one or more other such	step when the document is				
me	ans.	being obvious to a person skilled in t	the erf				
*P* document published prior to the international filing date but later than *&* document member of the same potent family the priority date claimed							
Date of the actual completion of the international search  Date of mailing of the international search report  15 DECEMBER 1998							
I Deciman III							
Commission Box PCT	nailing address of the ISA/US ner of Patents and Trademarks	Authorized officer  / Andrew Aldag	1. 1 10 m				
Washington, D.C. 20231   Facsimile No. (703) 305-3230   Telephone No. (703) 308-0661							

Form PCT/ISA/210 (second sheet)(July 1992)\*